



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09K 7/02, E21B 33/138, C08F 220/42		A1	(11) International Publication Number: WO 97/02330
			(43) International Publication Date: 23 January 1997 (23.01.97)
(21) International Application Number: PCT/US96/11021		Butternut Hollow, Acton, MA 01720 (US). ORKISZ, Michal [PL/US]; 12 Hatherly Road, Brighton, MA 02135 (US).	
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(30) Priority Data:		(81) Designated States: AU, BR, CA, MX, US, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
60/000,724 30 June 1995 (30.06.95) US 60/004,324 26 September 1995 (26.09.95) US 08/570,623 11 December 1995 (11.12.95) US 60/008,433 11 December 1995 (11.12.95) US 60/008,486 11 December 1995 (11.12.95) US		Published With international search report.	
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(54) Title: DRILLING COMPOSITIONS AND METHODS			
(57) Abstract			
<p>The materials include non-polyampholite crosslinked polymers and gels based on a polymer which in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water. The materials change their state of hydration in response to an environmental trigger. The disclosed materials are useful as drilling, completion or workover fluids in wells such as hydrocarbon producing wells. According to the disclosed method, crosslinked polymers or gels are introduced into a stratum, blocking or bridging the pores of the stratum. Thereafter, an environmental condition is changed to cause the hydrated material to become less hydrated to unblock the pores allowing production from the well.</p>			

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DRILLING COMPOSITIONS AND METHODS

This application claims benefit of priority of provisional application serial number 60/000,724, filed June 30, 1995, entitled, "Reversible Drilling Materials for Divalent Clear Drilling Fluids"; provisional application serial number 60/004,324, filed September 26, 1995, entitled "Reversible Drilling Materials for Divalent Clear Drilling Fluids"; U.S. serial number 08/570,623, filed December 11, 1995, entitled "Drilling Compositions and Methods"; provisional application serial number 60/008,433, filed December 11, 1995, entitled "Drilling Compositions and Methods"; and provisional application serial number 60/008,486, filed December 11, 1995, entitled "Gel Fluid Loss Control System for Drilling Applications".

Background of the Invention

This invention relates to drilling compositions and methods, and more particularly to drilling compositions useful in hydrocarbon well drilling operations which change from a more hydrated condition to a less hydrated condition in response to a change in an environmental condition.

During drilling of a well such as a well for extracting hydrocarbons, fluids are pumped into the well. Different fluids are used during different stages of the drilling operation. At one stage, fluids known as drilling and drill-in fluids are used. Such fluids serve several purposes such as cooling and lubricating the drill bit, and transporting solids to the surface.

Another important function of the drilling fluid is to balance the hydrostatic pressures encountered as the well is drilled. A condition called "blow-out" will occur if the pressure in an underground formation is greater than that provided by the fluid. In order to balance the pressures encountered in deep wells, fluids denser than water are typically required. One technique for increasing density is to create a brine or saturated salt solution which increases density up to 18 pounds per gallon.

To assure that a blow-out does not occur, the well is drilled in an over-balanced state, the pressure of the drilling fluid being higher than that

encountered in ~~the~~ formation. Such over-balanced ~~drilling~~ing, however, will cause the drilling fluid to infiltrate into the stratum which will damage the formation and greatly impair the ability to recover material from the well once production begins. Therefore, in the prior art, drilling fluids often

5 include solids known as bridging agents to serve as a barrier to prevent the drilling fluid from infiltrating into the formation pore spaces and thereby damaging the formation. One prior art technique is to suspend salt crystals in an already saturated salt or brine solution to bridge the formation pore spaces to prevent formation damage. See, U.S. Patent Nos.

10 4,186,803; 3,785,438; 3,878,141; 4,175,042; 4,369,843; and 4,822,500. Prior art bridging agents temporarily bridge over the formation pores rather than permanently plugging the pores. These bridging agents are dissolved when the workover or completion operation is accomplished to allow production from the well. A suspension agent is required to suspend the

15 salt crystals but prior art suspension agents such as xanthan gum work only in monovalent ion solutions such as sodium chloride and sodium bromide. Divalent ion solutions such as CaCl_2 and CaBr_2 have distinct advantages over the monovalent ion solutions, such as NaCl and NaBr . For example, a CaCl_2 solution can be made much denser than a NaCl

20 solution while maintaining a solids-free fluid. Further, the CaCl_2 is substantially cheaper than the NaBr at the same densities. The use of CaBr_2 raises the maximum density to 14.3 lbs/gallon while maintaining a solids-free fluid. A drilling fluid that uses these brines as a base fluid has long been sought, but there has been no material that could be added that

25 would have the necessary fluid-loss control and could be easily cleaned from the well.

Summary of the Invention

The following terms are used herein and are defined as follows. A

30 polymer is a long chain molecule with high molecular weight from a

sizeable number of repeat units. A crosslinked polymer is a polymer which contains crosslinking units joining the primary backbones of the polymer. A gel is a crosslinked polymer which is swollen with a significant quantity of fluid.

- 5 The invention, in a first aspect, is a copolymer comprising a first monomer whose homopolymer is hydrophobic but soluble in ionic solutions and a second monomer whose homopolymer is hydrophilic tending to swell in water. In one embodiment, the first monomer is a nitrile containing compound having a double or triple bond capable of
- 10 being polymerized and wherein the second monomer comprises acrylamides, substituted acrylamides, hydroxyacrylates or vinyl lactams having a double bond, triple bond or other functionality which can be polymerized. The first monomer may be selected from the group comprising acrylonitrile, methacrylonitrile, maleonitrile and fumaronitrile.
- 15 The second monomer may be selected from the group comprising acrylamide, methyl acrylamide, dimethyl acrylamide, ethyl acrylamide, 2-hydroxyethyl acrylate, hydroxypropyl acrylate and hydroxyethylmethyl acrylate or the group comprising vinyl lactams such as vinyl pyrrolidinone. A second monomer of the second type may be used to produce a
- 20 terpolymer.

- In another aspect, the invention is a non-polyampholite crosslinked polymer which polymer in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water. A polyampholite polymer is a polymer whose polymeric backbone contains, or pendant groups from
- 25 the polymeric backbone contain (in either ionized or neutral form) in substantial mole percentage both anionic groups, such as carboxylic acid or sulfonic acid and cationic groups such as quaternary ammonium groups. A crosslinked polyampholite polymer is a polyampholite polymer which contains cross-linking joining the primary polymer backbones. A
- 30 polyampholite gel is a crosslinked polyampholite polymer which is swollen

with a significant quantity of fluid. We have determined that the polyampholite gels described in the prior art (X. Yu, Ph.D. Thesis submitted to the Department of Physics, Mass. Inst. of Tech. 1993, which is included herein by reference) would not be useful for this application because they are too swollen in pure water or in dilute salt solutions (they do not collapse sufficiently) and because, although they expand in more concentrated salt solution relative to more dilute solutions, the degree of expansion is relatively small. In one embodiment, the non-polyampholite crosslinked polymer includes a monomer which forms a hydrophobic homopolymer and a monomer which forms a hydrophilic homopolymer which polymer in uncrosslinked form will be substantially soluble in ionic fluids and substantially insoluble in water. In this embodiment, the crosslinked polymer includes a first polymer which is a nitrile containing compound having a double or triple bond capable of being polymerized and wherein the second monomer comprises acrylamides, substituted acrylamides, hydroxy acrylates or vinyl lactams having a double bond, triple bond or other functionality which can be polymerized.

In yet another aspect, the invention is a gel comprising a non-polyampholite crosslinked polymer which polymer in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water, the crosslinked polymer being hydrated with an ionic fluid. In one embodiment, this gel comprises a monomer which forms a hydrophobic homopolymer and a monomer which forms a hydrophilic homopolymer, the gel being hydrated with an ionic fluid. The monomer which forms a hydrophobic homopolymer may be a nitrile containing compound which contains a double or triple bond capable of being polymerized and wherein the hydrophilic monomer comprises acrylamides, substituted acrylamides or hydroxyacrylates having a double bond, triple bond or other functionality which can be polymerized. Suitable monomers are set forth

above. The resulting material is soluble in ionic fluids such as calcium chloride but insoluble in water.

As used in this specification, an ionic fluid is an aqueous solution containing one or more of the following salts: NaCl, NaBr, CaCl₂, CaBr₂, ZnCl₂, ZnBr₂, RbCl, RbBr, CsCl, CsBr, Cs formate, Rb formate, K formate, Na formate, KBr, KCl, NH₄Cl, NH₄Br. A concentrated ionic fluid here is meant an ionic fluid which has a concentration greater than 6% dissolved salts by weight. An ionic fluid may, in addition, contain particulate material.

10 In one embodiment, the ionic fluid is a solution of a divalent cation such as calcium, magnesium or zinc. A suitable salt is selected from the group comprising calcium chloride and calcium bromide. In another embodiment, the aqueous salt solution is a solution of a monovalent cation. Suitable monovalent cationic systems are NaCl and NaBr. Other
15 suitable cationic systems include zinc, magnesium and potassium. In a preferred embodiment, the gel includes a crosslinked polymer of a first nitrile containing monomer and a second monomer selected from the group comprising acrylamides, substituted acrylamides and hydroxyacrylates, the crosslinked polymer hydrated with an aqueous
20 solution of calcium ions such as a solution of calcium chloride or calcium bromide. One suitable hydrated gel is selected to become dehydrated in water, in dilute sodium chloride or in potassium chloride. In yet another more general aspect of the invention, a crosslinked polymer hydrated with an ionic aqueous solution is selected to become less hydrated upon
25 exposure to an environmental condition. Suitable environmental conditions are temperature, pH, solvent, solvent concentration, ions, ionic concentration, electric field, magnetic field and pressure. These hydrated gels are effective drilling fluids.

In yet another aspect, the invention is a method for blocking and
30 unblocking pores of an underground stratum such as an oil-bearing

formation. The method includes introducing a gel as a treating fluid in a drilling, well completion or workover operation into the stratum to block or bridge the pores and exposing the gel to an environmental condition selected to lower the state of hydration of the gel, whereby the gel decreases in volume and unblocks the pores. Suitable gels comprise a crosslinked polymer other than a polyampholite polymer which polymer in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water, the crosslinked polymer being hydrated with an ionic fluid.

10 In yet another aspect of the invention, a method for drilling, well completion or workover includes introducing a gel hydrated with an ionic fluid into a subterranean formation and thereafter exposing the gel to an environmental condition selected to lower the state of hydration of the gel, whereby the gel decreases in volume to increase permeability of the well.

15 Suitable gels are those set forth above. Suitable ionic fluids are solutions of ions such as calcium, magnesium, sodium or zinc. Preferred solutions are solutions of calcium chloride, calcium bromide and zinc chloride. A suitable trigger for decreasing the state of hydration of the fluid is exposing the fluid to water, a dilute ammonium chloride solution or potassium

20 chloride solution typically 3 wt. %.

The gels of the invention hydrated, for example, with calcium chloride, have a suitable density for preventing blow-out in a well. Further, the hydrated gel will block or bridge the pores in a formation without allowing substantial amounts of the fluid to penetrate into the formation which would damage it. Upon exposure to an environmental condition such as contact with water or a dilute sodium or potassium chloride solution, the gel becomes less hydrated and shrinks in volume to unblock the pores to allow fluids in the stratum to be produced. When the stratum is a hydrocarbon bearing formation, the hydrocarbon will

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30 flow into the well for recovery.

Because fluids of the present invention are capable of utilizing calcium compounds, these fluids are more economical than monovalent ionic solutions such as sodium chloride and sodium bromide utilized in the prior art drilling fluids to increase density. Further, the materials of the invention are "clear" meaning that they do not include any solid materials such as calcium carbonate. It should also be noted that zinc chloride or zinc bromide, more expensive than calcium chloride or calcium bromide, can be used with the materials of the invention and allows for heavier fluids to be made for use in deeper wells where pressures are higher.

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Brief Description of the Drawing

Fig. 1 is a phase diagram of the acrylonitrile, acrylamide, 2-hydroxyacrylate system.

Fig. 2 is a cross-sectional view of a drilling rig and well.

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Description of the Preferred Embodiments

The polymers, crosslinked polymers and gels of the invention, sometimes referred to as Engineered Response™ materials, reversibly undergo a change from primarily hydrophilic to primarily hydrophobic in response to an environmental condition or trigger such as temperature, pH, solvent (such as hydrocarbons), solvent concentration, ions or ionic concentration, electric fields, magnetic fields or pressure. Materials and gels which exhibit such changes are known in the art. See, for example, Tanaka, *Physical Review Letters*, Vol. 40, No. 12, pp. 820-823 (1978); Tanaka, *Physical Review Letters*, Vol. 38, No. 14, pp. 771-774 (1978); Tanaka et al., *Physical Review Letters* 5, Vol. 45, p. 1636 (1980); Ilavsky, *Macromolecules*, Vol. 15, p. 782 (1982); Hrouz et al., *Europ. Polymer J.*, Vol. 17, p. 361 (1981); Ohmine et al., *J. Chem. Phys.*, Vol. 8, p. 6379 (1984); Tanaka et al., *Science*, Vol. 218, p. 462 (1982); Ilavsky et al., *Polymer Bull.*, Vol. 7, p. 107 (1982); Gehrke, *Responsive Gels: Volume Transitions II*; ed.

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K. Dusek, Springer-Verlag, New York, pp. 81-114 (1993); Li *et al.*, *Ann. Rev. Mat. Sci.*, 22; 243-277 (1992); Galaev *et al.*, *Enzyme Microb. Technol.*, 15, 354-366 (1993); Taylor *et al.*, *J. Polymer Sci.*, Vol. 13, 2551-2570 (1975); U.S. Patent No. RE35,068; and U.S. Patent Application serial number 5 08/393,971 filed February 24, 1995, entitled "Electromagnetically Triggered Responsive Gel Based Drug Delivery Device", all of which are incorporated herein by reference. The change from hydrophilic to hydrophobic character may be evidenced by a decrease in transmission of light (cloud point), change in viscosity or swelling or collapse. If a 10 responsive polymer undergoes change in response to a change in temperature, it is a "thermally responsive polymer" or a "temperature responsive polymer." If the responsive polymer undergoes the change in response to a change in pH, it is a "pH responsive polymer." The change in environmental condition which causes the hydrophobic/hydrophilic 15 change is called a "trigger." When an engineered response polymer or a "responsive polymer" is crosslinked to form a gel, the resulting material is designated an engineered response gel or a "responsive gel."

In one important aspect of the invention, the properties of engineered response or phase transition gels and/or polymers form a 20 system in which the gels and/or polymers will swell and block or bridge the pores of an underground hydrocarbon bearing stratum structure and then be triggered to change the state of hydration (solvation) of the gel or polymer to unblock the pores. A suitable trigger is the ionic strength of fluid to which the gel is exposed. Suitable materials will expand in a high 25 concentration of ions (high ionic strength) and collapse in a lower concentration of ions (lower ionic strength). An example is a material which will swell in the presence of concentrated calcium ions, such as are found in concentrated solutions of calcium chloride and/or calcium bromide (CaCl_2 or CaBr_2) and collapse in the presence of water or of a

dilute solution ions such as a solution of ammonium chloride or potassium chloride (NH_4Cl or KCl).

The responsive gels or polymers of the invention are made by creating a copolymer or terpolymer which will have the necessary responsive properties. The materials of the invention may be made from a first monomer whose homopolymer is hydrophobic (tends to collapse in water), but which will tend to wet, dissolve and/or expand in ionic solutions, particularly solutions of ions such as calcium, magnesium and zinc. Examples of such monomers are acrylonitrile, methacrylonitrile, maleonitrile, fumaronitrile or other nitrile containing monomers which contain a double or triple bond which can be polymerized.

A second monomer is one whose homopolymer is hydrophilic and will cause the gel or polymer to tend to swell in water giving it the pore bridging capability and necessary swelling capability in calcium chloride solution. Examples of suitable second monomers are acrylamides and substituted acrylamides, such as acrylamide, methyl acrylamide, dimethyl acrylamide and ethyl acrylamide; hydroxyacrylates such as 2-hydroxyethyl acrylate, hydroxypropyl acrylate and hydroxyethylmethyl acrylate; and vinyl lactams such as vinyl pyrrolidinone. All of these materials contain a double bond, triple bond or other functionality which can be polymerized. The synthesis methodology plays an important role in the material's ability to seal the formation. The material must be synthesized in a particle form in a controlled environment for it to be effective. Synthesizing the material in a bulk methodology results in a rubbery mass that is difficult to process to the correct size. The lack of good heat transfer also creates a very heterogeneous structure which adds to the material's inability to be processed to the correct size. A more preferable methodology would be one in which the gel is synthesized in particles of the correct size and has good heat transfer characteristics to provide a controlled reaction environment. That preferred methodology is inverse

suspension polymerization. A water solution of the polymer precursor is added to an oil phase and agitated. The agitation yields small particles, between 10 and 1000 μm , which upon reaction will remain as discrete particles even after the removal of agitation. The discrete particles are
5 added to a brine solution. The particles will swell in the brine solution and form a homogeneous solution.

The design of a polymer or gel useful in the present invention involves synthesizing a material which is a copolymer or terpolymer of the first monomer type and one or more monomers of the second monomer
10 type so that the hydrophobic and hydrophilic tendencies are balanced and the material will swell in concentrated calcium chloride or calcium bromide solution and collapse in water or in dilute sodium chloride or potassium chloride solution. It is possible to synthesize the materials of the invention utilizing one monomer of the first type as listed above and
15 allowing all or part of this monomer to react to form a material of the second monomer type. An example is the reaction of acrylonitrile with water to hydrolyze and form acrylamide. It is also contemplated that the monomers of the first and second type will comprise a block or graft copolymer form so that the arrangement of the first monomer and second
20 monomer in the polymer or gel is not random.

Examples

Example 1: Synthesis of Acrylonitrile /2-Hydroxyethyl Acrylate Gels in $\text{CaBr}_2/\text{ZnCl}_2$.

25 650 grams of calcium bromide hydrate (Aldrich, 98%) is added to 500 ml of DI (deionized) water and allowed to dissolve. 90 ml of this solution is placed in an Erlenmeyer flask. 1583 grams of zinc chloride (Aldrich, 98%, A.C.S. reagent) is added to 500 ml of DI water and allowed to dissolve. Ten ml of this solution is added to the 90 ml of CaBr_2
30 solution in the Erlenmeyer. 3.6956 grams (4.59 ml) of acrylonitrile

(Aldrich, 99%), 8.0878 grams (8.00 ml) of 2-hydroxyethyl acrylate (Aldrich, 96%) and 0.1498 grams (0.144 ml) of diethylene glycol diacrylate (Monomer-Polymer & Dajac Laboratories, Catalogue No. 7945) are added to the 100 ml of $\text{CaBr}_2/\text{ZnCl}_2$ solution. The flask is sealed with a rubber stopper and N_2 is bubbled through the solution for 30 minutes. In a 20 dram glass vial, 0.144 grams of VA-086 (Wako Chemicals USA, Inc.) is added to 10 ml of DI water and allowed to dissolve. The VA-086 serves as an initiator. Using a syringe, 5 ml of the VA-086 solution is added to the flask containing the reactants. The flask is swirled until well mixed and placed in an oven at 80°C overnight to allow the gel to form.

Example 2: Synthesis of Acrylonitrile/2-Hydroxyethyl Acrylate Gels in CaBr_2 .

650 grams of calcium bromide hydrate (Aldrich, 98%) is added to 500 ml of DI water and allowed to dissolve. 100 ml of this solution is placed in an Erlenmeyer flask. 3.6956 grams (4.59 ml) of acrylonitrile (Aldrich, 99%), 8.0878 grams (8.00 ml) of 2-hydroxyethyl acrylate (Aldrich, 96%), and 0.1498 grams (0.144 ml) of diethylene glycol diacrylate (Monomer-Polymer & Dajac Laboratories, Catalogue No. 7945) are added to the 100 ml of CaBr_2 solution. The flask is sealed with a rubber stopper and N_2 is bubbled through the solution for 30 minutes. In a 20 dram glass vial, 0.144 grams of VA-086 is added to 10 ml of DI water and allowed to dissolve. Using a syringe, 5 ml of the VA-086 solution is added to the flask containing the reactants. The flask is swirled until well mixed and placed in an oven at 80°C overnight to allow the gel to form.

Example 3: Synthesis of Acrylonitrile/Acrylamide/2-Hydroxyethyl Acrylate Gels.

650 grams of calcium bromide hydrate (Aldrich, 98%) is added to 500 ml of DI water and allowed to dissolve. 100 ml of this solution is

placed in an Erlenmeyer flask. 2.9565 grams (3.67 g) of acrylonitrile (Aldrich, 99%), 1.9803 grams of acrylamide (Aldrich, 99%), 6.4702 grams (6.40 ml) of 2-hydroxyethyl acrylate (Aldrich, 96%), and 0.1498 grams (0.144 ml) of diethylene glycol diacrylate (Monomer-Polymer & Dajac Laboratories, Catalogue No. 7945) are added to the 100 ml of CaBr_2 solution. Heat may be necessary to dissolve the acrylamide in the CaBr_2 solution. The flask is sealed with a rubber stopper and N_2 is bubbled through the solution for 30 minutes. In a 20 dram glass vial, 0.144 grams of VA-086 is added to 10 ml of DI water and allowed to dissolve. Using a syringe, 5 ml of the VA-086 solution is added to the flask containing the reactants. The flask is swirled until well mixed and placed in an oven at 80° C overnight to allow the gel to form.

Example 4: Testing of Acrylonitrile/2-Hydroxyethyl Acrylate Gels.

400 grams of CaCl_2 (Aldrich Catalogue No. 22,231-3) is added to 600 ml of DI water and allowed to dissolve and cool. The terpolymer gel synthesized in Example 2 is removed from the flask and added to 400 ml of the CaCl_2 solution. The mixture is allowed to swell for 24 hours and then homogenized (Arde-Barinco Inc., CJ-4 16" Laboratory Mixer) for 5 minutes on the "up" mode at 40% motor RPM. Using the Permeability Plugging Apparatus (PPA, Fann Instrument Company, Part No. 382020001) the gel mixture is tested using a 10 μm ceramic filter. The test consists of adding approximately 300 ml of the mixture to the cell unit, sealing the cell, placing it into the heating jacket, applying 100 psi of back pressure using N_2 , heating to the desired testing temperature, and applying 500 psi of hydraulic pressure (procedure for testing found in the Fann PPA manual). The amount of filtrate that penetrates through the ceramic disc in 30 minutes is the test result. The test showed 18 ml over the required 30 minutes at a temperature of 200° F. Using the same disc, the cell is further heated to 250° F and 45 ml of filtrate penetrated in 2 minutes.

Example 5: Testing of Acrylonitrile/Acrylamide/2-Hydroxyethyl Acrylate Gels.

400 grams of CaCl_2 (Aldrich Catalogue No. 22,231-3) is added to 600 ml of DI water and allowed to dissolve and cool. The terpolymer gel synthesized in Example 2 is removed from the flask and added to 400 ml of the CaCl_2 solution. The mixture is allowed to swell for 24 hours and then homogenized (Arde-Barinco Inc., CJ-4 16" Laboratory Mixer) for 5 minutes on the "up" mode at 40% motor RPM. Using the Permeability Plugging Apparatus (PPA, Fann Instrument Company, Part No. 382020001) the gel mixture is tested using a 10 μm ceramic filter. The test consists of adding approximately 300 ml of the mixture to the cell unit, sealing the cell, placing it into the heating jacket, applying 100 psi of back pressure using N_2 , heating to the desired testing temperature, and applying 500 psi of hydraulic pressure (procedure for testing found in the Fann PPA manual). The amount of filtrate that penetrates through the ceramic disc in 30 minutes is the test result. The test showed 15 ml over the required 30 minutes at a temperature of 200° F. Using the same disc, the cell is further heated to 250° F and 6 ml of filtrate penetrated in 30 minutes. At 300° F, 11 ml of filtrate penetrated in 10 minutes. To test reversibility of the material, the material is tested on an API filter press (Fann Instrument Company, Part No. 30200). Approximately 200 ml of mixture is placed in the cell and a pressure of 100 psi is applied, using N_2 gas, for ten minutes to assure that a block is achieved with a ten micron disc. The excess mixture is then removed and approximately 300 ml of 3% potassium chloride (also may use 3% ammonium chloride) is added. The amount of filtrate that penetrates through the disc in a designated time frame is the reverse test result. The test showed 150 ml of filtrate over 6 minutes.

Example 6: Synthesis of Acrylonitrile/Acrylamide/2-Hydroxyethyl Acrylate Gels.

250 ml warm 14.2 lbs/gallon Calcium Bromide solution (Baroid Drilling Fluids) is placed in an Erlenmeyer flask. 4.938 grams of acrylamide (Aldrich, 99%) is allowed to dissolve. This solution is then placed in a sep funnel and 7.7457 grams (9.61 ml) of acrylonitrile (Aldrich, 99%), 16.135 grams (15.96 ml) of 2-hydroxyethyl acrylate (Aldrich, 96%), and 0.5618 grams (0.540 ml) of diethylene glycol diacrylate (Monomer-Polymer & Dajac Laboratories, Catalogue No. 7945) are added. N₂ is bubbled through the solution for 30 minutes. In a 40 dram glass vial, 0.378 grams of V-50 Azo initiator (Wako Chemicals USA, Inc.) is added to 28 ml of DI water and allowed to dissolve. 12.5 ml of the V-50 solution is then added to the calcium bromide solution and the solution is degassed for an additional 15 minutes. In a 500 ml baffled three necked reaction vessel, 400 ml of Norpar-12 (Exxon), with .75 g of Span 80 (sorbitan monooleate, ICI Americas, Inc.), is degassed for 45 minutes, while the norpar is being stirred with a six bladed R100 impeller, at 560 RPM. The calcium bromide solution is then added to the norpar solution, which is still being stirred, and the reaction runs for 15-18 hours, at approximately 70° C.

Example 7: Testing of Acrylonitrile/Acrylamide/2-Hydroxyethyl Acrylate Gels.

The terpolymer beads synthesized in Example 6 are removed from the suspension vessel and centrifuged at 3/4 speed on a IEC HN-SII centrifuge for 30 minutes. The norpar is decanted off and the beads removed. Approximately 190 g of beads are added to 556 g of the CaCl₂ solution (11.6 lbs/gallon from Baroid Drilling Fluids, Inc.). The mixture is allowed to swell for 16 hours, stirring with an A-310 impeller at 500-600 rpm. Using the Permeability Plugging Apparatus (PPA, Fann Instrument Company, Part No. 382020001) the gel mixture is tested using a 10 μm ceramic filter. The test consists of adding approximately 350 ml of the

mixture to the unit, sealing the cell, placing it the heating jacket, applying 100 psi of back pressure using N_2 , heating to the desired testing temperature, and applying 500 psi of hydraulic pressure (procedure for testing found in the Fann PPA manual). The amount of filtrate that
5 penetrates through the ceramic disc in 30 minutes is the test result. The test showed 2.5 ml over the required 30 minutes at a temperature of 250° F.

To test reversibility of this material, it is diluted with DI water, using a 1:5 ratio. The material dehydrates, turning white. The collapsed
10 material no longer is suspended in solution.

When zinc chloride ($ZnCl_2$) solution alone is present, the homopolymer polyacrylonitrile (PAN) demonstrates the desired properties of blocking a porous medium and then dehydrating in water. It is noted that PAN is soluble in $ZnCl_2$ but not in water. The PAN gel prevented
15 $ZnCl_2$ solution from passing through a filter by effectively blocking the pores of the filter. When water was added, the gel collapsed, unblocking the pores and allowed water to pass through the filter.

There are, however, cost, corrosivity and environmental concerns connected with zinc chloride solutions. A drilling solvent which addressed
20 these concerns is a solution of $CaCl_2$ and $CaBr_2$ in water. We have observed that the homopolymer PAN is not soluble in either of these. If enough $ZnCl_2$ is added to the solvent, PAN will become soluble as shown in Example 1. To eliminate the need for zinc, a copolymer of acrylonitrile was synthesized and tested. If the correct comonomer is chosen, the
25 solubility of the copolymer in the $CaCl_2$ or $CaBr_2$ solution is achieved while preserving the lack of solubility of the copolymer in water. See examples 2 and 4 above. This property has been demonstrated with acrylamide, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethylmethyl acrylate, dimethyl acrylamide and vinyl
30 pyrrolidinone. Any hydrophilic monomer of which the polymer is

soluble in CaCl_2 or CaBr_2 would be suitable if synthesized in correct ratio with the acrylonitrile and if the resulting polymer has a necessary performance and is thermally stable and otherwise suitable for use in the intended application.

- 5 It has been found that the desired performance can be achieved and enhanced by adding a third monomer to the polymer backbone to form a terpolymer. This often increases operating temperature range while preserving the reversing capability of the material. A terpolymer may be synthesized out of two monomers of the second type discussed above and
10 one monomer of the first type listed above and would have the desired properties. The acrylonitrile provides the reversibility in water or low ionic strength solvents (3 wt% KCl), while the other monomers supply the solubility in CaCl_2 or CaBr_2 for example. There is no reason to believe that it would not be possible to add more hydrophilic monomers to
15 polymerize with acrylonitrile to achieve the desired effects. See, examples 3 and 5.

From the experiments set forth above, certain conclusions can be drawn. The hydration state of the polymer has a direct effect on its filtration properties which are important in preventing damage to an oil-
20 bearing formation, for example. Therefore, if one can control the hydration state of the gel, one can control the filtration properties of the gel. The hydration properties of the gel can be modified by copolymerizing monomers with different hydrophobic/hydrophilic characteristics. By adjusting the ratio of the monomers, one can radically
25 affect the solubility in related solvents like water and concentrated salt solutions. The materials of the invention enable the use of $\text{CaCl}_2/\text{CaBr}_2$ in production zone drilling.

The materials of the invention can also be made by modifying an acrylonitrile gel. By hydrolyzing portions of an acrylonitrile gel one can
30 achieve the same effect as copolymerizing the two monomers together.

The copolymerization is simpler on the lab scale but post-treatment on the commercial scale may be more economical. As discussed above, a suitable trigger to remove the blocking material will be water or another solution in which the gel has been designed to collapse such as dilute sodium chloride or potassium chloride.

The phase diagram of Fig. 1 delineates some conclusions in the acrylonitrile, acrylamide, 2-hydroxyethyl acrylate (AN/AAm/HEA) system. The phase diagram of Fig. 1 is exemplary only in illustrating a way of selecting proportions of the monomers in making a suitable terpolymer. The section near the top vertex represents a region in which the gels do not swell in calcium chloride. The lower segment which contains the AAm and HEA vertices represents the region in which the gels will not collapse in water or dilute saline. The numerical values in Fig. 1 represent maximum measured Fahrenheit temperature at which the gel will hold back fluid in testing. In Fig. 1, optimal materials illustrated by the phase diagram are in the range of 40% AN/20% AAm/40% HEA and 50% AN/10% AAm/40% HEA. Suitable compositions are between 35% and 55% AN, between 5% and 25% AAm and between 30% and 50% HEA. The characteristics of a number of gel combinations are shown in Table 1.

Table 1

Sample No.	AN/AMIDE/HEA Ratio	Syn. Solvent	Pressure/Temp	ml/min	Reversibility
1	0/0/100	water	500, 200° F	48 ml/30 min.	does not reverse
2	10/0/90	water	500, 250° F	.8 ml/10 min.	does not reverse
3	15/0/85		500, 200° F	21.5 ml/30 min.	does not reverse
4	50/0/50	CaBr ₂	500, 200° F	18 ml/30 min.	reverses

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Sample No.	AN/AMIDE/HEA Ratio	Syn. Solvent	Pressure/Temp	ml/min	Reversibility
	"		500, 250° F	45 ml/30 min.	
5	0/50/50	water	500, 200° F	12 ml/30 min.	does not reverse
	"		500, 250° F	6 ml/30 min.	
	"		500, 330° F	50 ml/5 min.	
6	10/90/0	water	500, 200° F	97 ml/4 min.	does not reverse
7	15/85/0	water	500, 200° F	88 ml/4 min.	does not reverse
8	10/45/45	water	500, 200° F	8 ml/30 min.	does not reverse
	"		500, 250° F	.8 ml/10 min.	
	"		500, 300° F	2.7 ml/10 min.	
	"		500, 330° F	7.5 ml/10 min.	
9	50/10/40 (.5% XL)	CaBr ₂	500, 200° F	10 ml/30 min.	reverses
	"		500, 250° F	25 ml/10 min.	
10	50/10/40 (1% XL)	CaBr ₂	500, 200° F	49 ml/30 min.	reverses
11	50/40/10	CaBr ₂	500, 200° F	did not test	viscous liquid
12	50/25/25	CaBr ₂	500, 200° F	failed at 200° F	
13	40/20/40 (hom 5 min.)	CaBr ₂	500, 200° F	15 ml/30 min.	reverses
	"		500, 250° F	6 ml/30 min.	
	"		500, 300° F	11 ml/10 min.	
14	40/20/40 (ho, 1 hr.)	CaBr ₂	500, 200° F	59 ml/10 min.	

Sample No.	AN/AMIDE/HEA Ratio	Syn. Solvent	Pressure/Temp	ml/min	Reversibility
15	33/33/33	CaBr ₂	500, 200° F	20 ml/30 min.	appears not reversible
			500, 250° F	6 ml/30 min.	
			500, 310° F	6 ml/10 min.	
	all gels made in water	were homog.	1 hour		
5	*all gels made in water	were homog.	5 min., unless	Noted*	

Though the AN/AAm/HEA performs well, it lacks the required long-term stability. The HEA protons of the gel will hydrolyze to acrylic acid in less than 24 hours at 250°F. The acrylic acid does not have the required solubility in the divalent brines and the polymer precipitates. As stated in U.S. Patent No. 5,035,812, vinyl lactams have excellent thermal stability even in the divalent brines, particularly calcium. The vinyl pyrrolidinone can be substituted for the HEA and increase the stability of the gel at 250°F substantially. This is very important as the drilling fluid must continue to function for days at the elevated temperature.

In addition to performing at elevated temperatures, the material must also perform under the other system requirements such as shear. One way to accomplish having a material perform long-term under these conditions is to have the system modify the material to optimize its performance. Given an understanding of the material and the system, one skilled in the arts can accomplish this. For instance under shear simulation tests the gel material may break into smaller pieces. The rate of breakage is determined by the degree of crosslinking in the material. By adding materials with different amounts of crosslinker, see examples 8 through 11, the material changes under shear, but the performance remained

unchanged during the duration of the test (see table below). The shear test was conducted on a multi-mixer (Fann Instruments) and the PPT was conducted at 500 psi and on a 20 μ m disc.

5	Shear Time	30 minute volume
	Initial	21 - 22 ml
	3 hours	23 - 26 ml
	6 hours	28 ml

Adding materials of different crosslinking can also increase the scaling performance. For instance, adding a material with high crosslinking and a material with low crosslinking can create a system that acts a lot like the conventional materials, i.e., sized salt and HEC. The harder material, higher crosslinked material, will form a gross seal while the softer material, the lower crosslinked material, will form the fine seal. Both materials will still have the required reversing characteristics.

Examples of gels including vinyl pyrrolidinone follow.

Example 8: Synthesis of Acrylonitrile/Acrylamide/1-Vinyl-2-Pyrrolidinone Gels.

9.95 grams of acrylamide (Aldrich, 99%) is allowed to dissolve in 145 ml H₂O. This solution is then placed in a separatory funnel and 18.57 grams (23.04 ml) of acrylonitrile (Aldrich, 99%) and 23.34 grams (22.44 ml) of 1-vinyl-2-pyrrolidinone (Aldrich, 99%) are added. To this the appropriate amount of methylenebisacrylamide (Aldrich, 99%) is added (see following table).

<u>Bis XL% of mM Conc.</u>	<u>Bis Solution (g/ml H₂O)</u>	<u>amount added</u>
.01%	(.1 g/10 ml)	1.08 ml
.05%	(.1 g/10 ml)	5.40 ml
.50%	(.54 g/40 ml)*	add all
*subtract 40 ml from initial H ₂ O amount		

5 N₂ is bubbled through the solution for 25 minutes. In a 20 dram glass vial, 0.374 grams of V-50 Azo initiator (Wako Chemicals USA, Inc.) is added to 12 ml of DI water and allowed to dissolve. 5.0 ml of the V-50
 10 solution is then added to the aqueous solution and the solution is degassed for an additional 5 minutes. In a 500 ml baffled three necked reaction vessel, 300 ml of Norpar-12 (Exxon), with 1.5 g of Ganex V216 (ICI Americas, Inc.) is heated for approximately 3 hours. The Norpar is
 15 degassed during the final 55 minutes of heating, while being stirred with a three bladed A200 impeller, at 435 RPM. The aqueous solution is then added to the Norpar solution, which is still being stirred, and the reaction runs for 15-18 hours, at 60 - 70° C.

20 Example 9: Testing Blocking Ability of Acrylonitrile/Acrylamide/1-Vinyl-2-Pyrrolidinone Gels.

The terpolymer beads synthesized in Example 8 are separated from the Norpar. These beads are then swollen in a pure or diluted CaCl₂ solution (11.6 lb/gallon from Baroid Drilling Fluids, Inc.) for approximately 16 hours, stirring with an A-310 impeller at 400 - 500 rpm.
 25 These mixtures are then tested for blocking capability on 10, 20 and 35 μm ceramic filters, using the Permeability Plugging Apparatus (PPA, Fann Instrument Company, Part No. 382020001). The procedure for testing is described in the earlier examples. The amount of filtrate that penetrates

through the ceramic disc in 30 minutes is the test result. The following Table lists results for various combinations of beads, swollen in 647 g CaCl_2 , along with results after shearing the particles on a multi-mixer for different periods of time. The results below hold for density ranges between 10.5 lb/gallon to 11.5 lb/gallon.

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<u>Trial No.</u>		<u>Beads</u> <u>.01%</u>	<u>Beads</u> <u>.05%</u>	<u>Beads</u> <u>.5%</u>	<u>Disc Size</u>	<u>Shear</u> <u>Time</u>	<u>ml in 30 min</u>
I	ratio	100			20 μm	0	10 -15 ml
	grams	56				1 hour	no control
II	ratio		100		20 μm	0	40 ml
	grams		56			1 hour	40 ml
						3 hours	no control
III	ratio			100	20 μm	0	100 ml/20 min
	grams			56		1 hour	100 ml/20 min
						3 hours	100 ml/20 min
IV	ratio	30	30	40	10 μm	0	9 ml
	grams	17	17	22	20 μm	0	18 - 22 ml
						1 hour	23 - 26 ml
						3 hours	23 - 26 ml
						6 hours	26 - 28 ml
					35 μm	0	40 ml

Example 10: Testing Reversibility of Acrylonitrile/Acrylamide/1-Vinyl-2-Pyrrolidinone Gels.

The terpolymer is tested using the API filter press (Baroid Drilling Fluids, Inc.) for blocking capability. Approximately 250 ml of material is placed in the cell containing a 20 μm disc and 100 psi of pressure is applied. The amount of filtrate that penetrates through the ceramic disc in a specified period of time is the test result. The material is then removed and 100 psi of pressure is applied to assure the seal is still present on the ceramic disc. Water is then added to the cell and again 100 psi of pressure

is applied. The Table below lists the results. As shown, the material loses its blocking capability when water is added.

Trial No.	Disc Size	Initial Block (ml/30 min)	Reverse with H ₂ O (ml/min)
I	20 μ m	20 ml	520 ml/27 min

Example 11: Testing Thermal Stability of Acrylonitrile/Acrylamide/1-Vinyl-2-Pyrrolidinone Gels.

The terpolymer, swollen in CaCl₂ solution, is placed in a thermal pressure cell (Baroid Drilling Fluids, Inc.), at a selected temperature, for varying periods of time. In order to test thermal stability, the terpolymer is removed from the pressure cell and retested on the PPA, using the procedure outline above. The Table below lists the results.

Trial No.	Formulation of Material	Temp.	Time	Disc Size	ml in 30 min
I	35/30/35 AN/Aam/VP	ambient	0 days	20 μ m	20 ml
	0.1% BIS	200° F	2 days	20 μ m	26 ml
		200° F	11 days	20 μ m	20 ml
II	50/20/30 AN/Aam/VP	ambient	0 days	20 μ m	15 ml
	.01% BIS	200° F	4 days	20 μ m	~ 40 ml
IV	50/20/30 AN/Aam/VP	ambient	0 days	20 μ m	29 ml
	.01% BIS(30%); .05% BIS (70%)	250° F	3 days	20 μ m	34 ml
		250° F	7 days	20 μ m	60 ml
V	50/20/30 AN/Aam/VP	ambient	0 days	20 μ m	22 ml
	.01% BIS(30%); .05% BIS (30%)	250° F	4 days	20 μ m	26 ml
	.5% (40%)	250° F	6 days	20 μ m	32 ml

The wellbore filling methods of the invention are illustrated in Fig. 2. In Fig. 2, drilling rig 11 is disposed on top of a borehole 12. An annulus 16 is created between the borehole 12 and drill string 18. A drill bit 22 is disposed at the lower end of drill string 18 and carves the borehole 12 out of earth formations 24. A metal surface casing 29 is positioned in the borehole 12 above the drill bit 22 for maintaining the integrity of the borehole 12 near the surface. The fluids 26 of the invention may be kept in a mud pit 34 and pumped by a pumping system 30 through a conduit 31 into the central axial passageway of the drill string 18. The fluid 26 exits the drill string 18 at the drill bit 22 and travels back up the annulus 16. The material then flows through a conduit 32 into the mud pit 34.

As discussed above, the fluid 26 will bridge pores in the earth formation 24 to prevent formation damage. When desired, a substance such as water or an aqueous solution of sodium chloride or potassium chloride is pumped out of the mud pit 34, through the drill string 18 and out through the bit 22 into the annulus 16 to lower the state of hydration of the polymer or crosslinked polymer fluid 26 so that it decreases in volume to remove the bridge and seal from the formation 24 to allow the flow of fluids from the formation into the borehole 12.

It is intended that all variations and modifications of the inventions set forth above be included within the scope of the appended claims.

What is claimed is:

1. A α -polyampholite crosslinked polymer which polymer in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water.

5 2. The crosslinked polymer of claim 1 comprising a first monomer which forms a hydrophobic homopolymer and a second monomer which forms a hydrophilic homopolymer which polymer in uncrosslinked form will be substantially soluble in ionic fluids and substantially insoluble in water.

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3. The crosslinked polymer of claim 1 in which the ionic fluids comprise concentrated ionic fluids.

4. The crosslinked polymer of claim 2 wherein the first
15 monomer comprises a nitrile containing compound which contains a double or triple bond capable of being polymerized and wherein the second monomer comprises acrylamides, substituted acrylamides, hydroxyacrylates or vinyl lactams having a double bond, triple bond or other functionality which can be polymerized.

20

5. The crosslinked polymer of claim 4 wherein the first monomer is selected from the group comprising acrylonitrile, methacrylonitrile, maleonitrile and fumaronitrile.

25 6. The crosslinked polymer of claim 4 wherein the second monomer is selected from the group comprising acrylamide, methyl acrylamide, dimethyl acrylamide, ethyl acrylamide, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethylmethacrylate and 1-vinyl 2-pyrrolidinone.

30

7. Comprising a non-polyampholite crosslinked polymer which polymer in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water.

5 8. The gel of claim 7 comprising a monomer which forms a hydrophobic homopolymer and a monomer which forms a hydrophilic homopolymer which polymer in uncrosslinked form will be substantially soluble in ionic fluids and substantially insoluble in water, the crosslinked polymer being hydrated with an ionic fluid.

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 9. The gel of claim 8 further comprising 2 monomers which form hydrophilic homopolymers.

 10. The gel of claim 7 in which the ionic fluid comprises
15 concentrated ionic fluid.

 11. The gel of claim 8 or claim 9 wherein the monomer which forms a hydrophobic homopolymer is a nitrile containing compound which contains a double or triple bond capable of being polymerized and
20 wherein the hydrophilic monomer comprises acrylamides, substitute acrylamides, hydroxyacrylates or vinyl lactams having a double bond, triple bond or other functionality which can be polymerized.

 12. The gel of claim 11 wherein the monomer which forms a
25 hydrophobic homopolymer is selected from the group comprising acrylonitrile, methacrylonitrile, maleonitrile and fumaronitrile.

 13. The gel of claim 11 wherein the monomer which forms a hydrophilic homopolymer is selected from the group comprising
30 acrylamide, methylacrylamide, dimethyl acrylamide, ethyl acrylamide, 2-

hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxyethylmethyl acrylate and 1-vinyl-2-pyrrolidinone.

14. The gel of claim 7 wherein the ionic fluid comprises one or
5 more divalent ions.

15. The gel of claim 7 wherein the ionic fluid comprises calcium, magnesium or zinc ions.

10 16. The gel of claim 7 wherein the ionic fluid comprises calcium chloride or calcium bromide.

17. The gel of claim 7 adapted to collapse (become dehydrated) upon exposure to an environmental condition.

15

18. The gel of claim 17 wherein the environmental condition is selected from the group comprising temperature, pH, solvent, solvent concentration, ions, ionic concentration, electric field, magnetic field and pressure.

20

19. The gel of claim 17 in which the environmental condition is exposure to water or a dilute ionic fluid.

20. The gel of claim 17 in which the environmental condition is
25 exposure to water, dilute sodium chloride, dilute potassium chloride or dilute ammonium chloride.

21. A polymer comprising approximately 35% to 55% of a first monomer which forms a hydrophobic homopolymer, approximately 5%
30 to 25% of a second monomer which forms a hydrophilic homopolymer

and approximately 30 to 50% of a third monomer which forms a hydrophilic homopolymer.

22. The polymer of claim 21 wherein the first monomer is acrylonitrile, the second monomer is acrylamide and the third monomer is 2-hydroxyethylacrylate.

23. The polymer of claim 21 which is crosslinked.

24. The polymer of claim 23 hydrated to form a gel.

25. Method for blocking and unblocking pores of an underground stratum comprising:

introducing a hydrated gel into the stratum to block the pores; and exposing the gel to an environmental condition selected to lower the state of hydration of the gel whereby the gel decreases in volume and unblocks the pores.

26. Well drilling method comprising:

introducing a gel hydrated with an ionic fluid into an underground stratum during drilling; and

exposing the gel to an environmental condition selected to lower the state of hydration of the gel whereby the gel decreases in volume to increase the permeability of the underground stratum into the well.

25

27. The method of claim 25 or claim 26 wherein the gel comprises the gel of claim 7, claim 8, claim 9, claim 11, claim 12, claim 13, claim 14, claim 15, claim 16, claim 17, claim 18, claim 20 or claim 21.

28. The method of claim 25 or claim 26 wherein the gel being hydrated with an ionic fluid comprises a non-polyampholite crosslinked polymer which polymer in uncrosslinked form is substantially soluble in ionic fluids and substantially insoluble in water.

5

29. The method of claim 28 wherein the crosslinked polymer comprises a monomer which forms a hydrophobic homopolymer and a monomer which forms a hydrophilic homopolymer which polymer in uncrosslinked form will be substantially soluble in ionic fluids and substantially insoluble in water, the crosslinked polymer being hydrated with an ionic fluid.

30. The method of claim 28 wherein the monomer which forms a hydrophobic homopolymer comprises a nitrile containing compound which contains a double or triple bond capable of being polymerized and wherein the monomer which forms a hydrophilic homopolymer comprises acrylamides, substituted acrylamides or hydroxyacrylates having a double bond, triple bond or other functionality which can be polymerized.

31. The method of claim 30 wherein the monomer which forms a hydrophobic homopolymer is selected from the group comprising acrylonitrile, methacrylonitrile, maleonitrile and fumaronitrile.

32. The method of claim 30 wherein the monomer which forms a hydrophilic homopolymer is selected from the group comprising acrylamide, methyl acrylamide, dimethyl acrylamide, ethyl acrylamide, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethylmethacrylate and 1-vinyl-2-pyrrolidinone.

33. The method of claim 25 or 26 wherein the ionic fluid comprises ions selected from the group comprising calcium, magnesium or zinc.

5 34. The method of claim 33 wherein the ionic fluid comprises calcium ions.

35. The method of claim 25 or 26 wherein the environmental condition comprises exposure to water, non-concentrated sodium chloride,
10 non-concentrated potassium chloride, or non-concentrated ammonium chloride.

36. The method of claim 25 or 26 wherein the environmental condition is a change in pH.

15

37. Hydrocarbon well drilling method comprising:
introducing into an underground hydrocarbon bearing stratum during drilling a gel comprising the gel of claim 7 and exposing the hydrated gel to a dilute saline solution to lower the state of hydration of
20 the gel whereby the gel decreases in volume to increase the permeability of the underground stratum into the well.

38. Well completion and workover method comprising:
pumping a treating fluid comprising the gel of claim 7 into the well;
25 contacting the treating fluid with a subterranean formation to form a bridge and seal on the formation to bridge and seal off the formation pores;
and

pumping a substance into the well for contact with the gel, the
30 substance selected to lower the state of hydration of the gel whereby the

gel decreases in volume to remove the bridge and seal from the formation to allow the flow of fluids from the formation into the well.

39. The method of claim 38 wherein the substance is selected
5 from the group comprising water, sodium chloride solution, potassium
chloride solution or ammonium chloride solution.

40. The polymer of claim 21 wherein the first monomer is
acrylonitrile, the second monomer is acrylamide and the third monomer is
10 1-vinyl-2-pyrrolidinone.

41. The materials of any of claims 1-24 in particulate form.

42. The materials of claim 41 wherein the particles are in the size
15 range 10 - 1000 μm .

FIG. 1

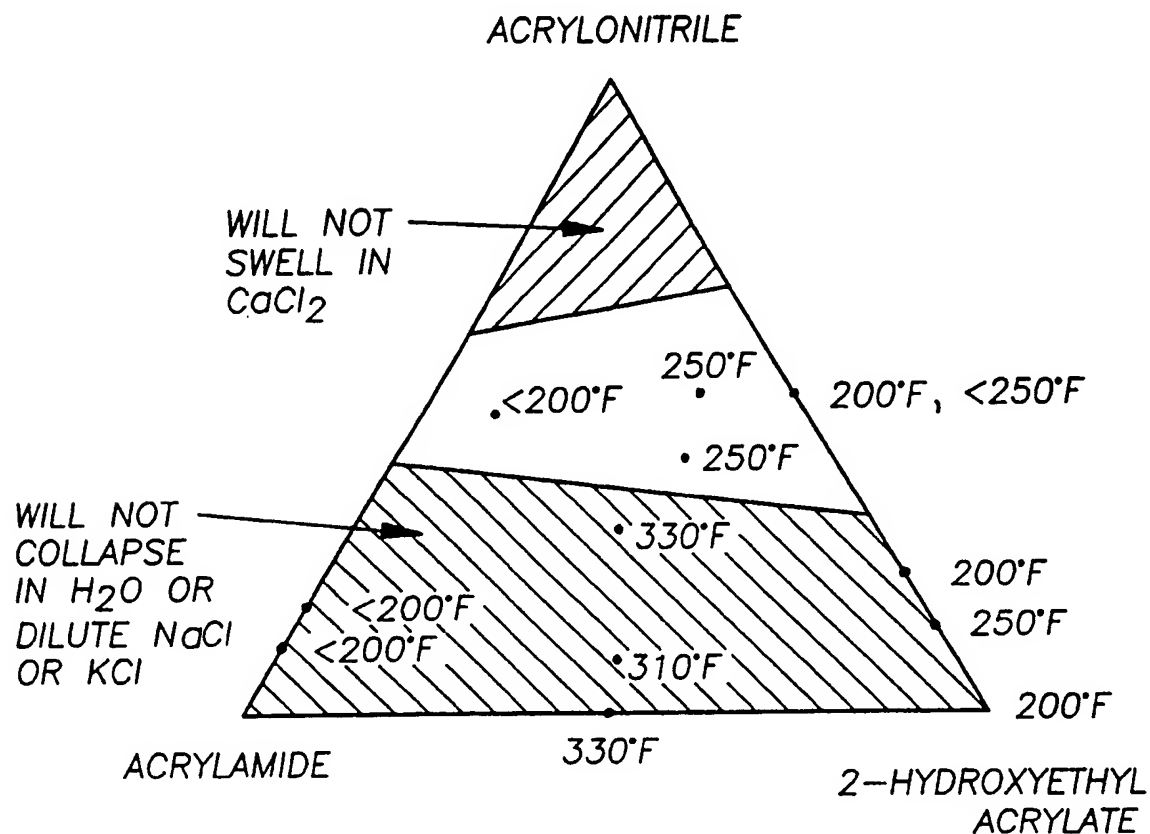
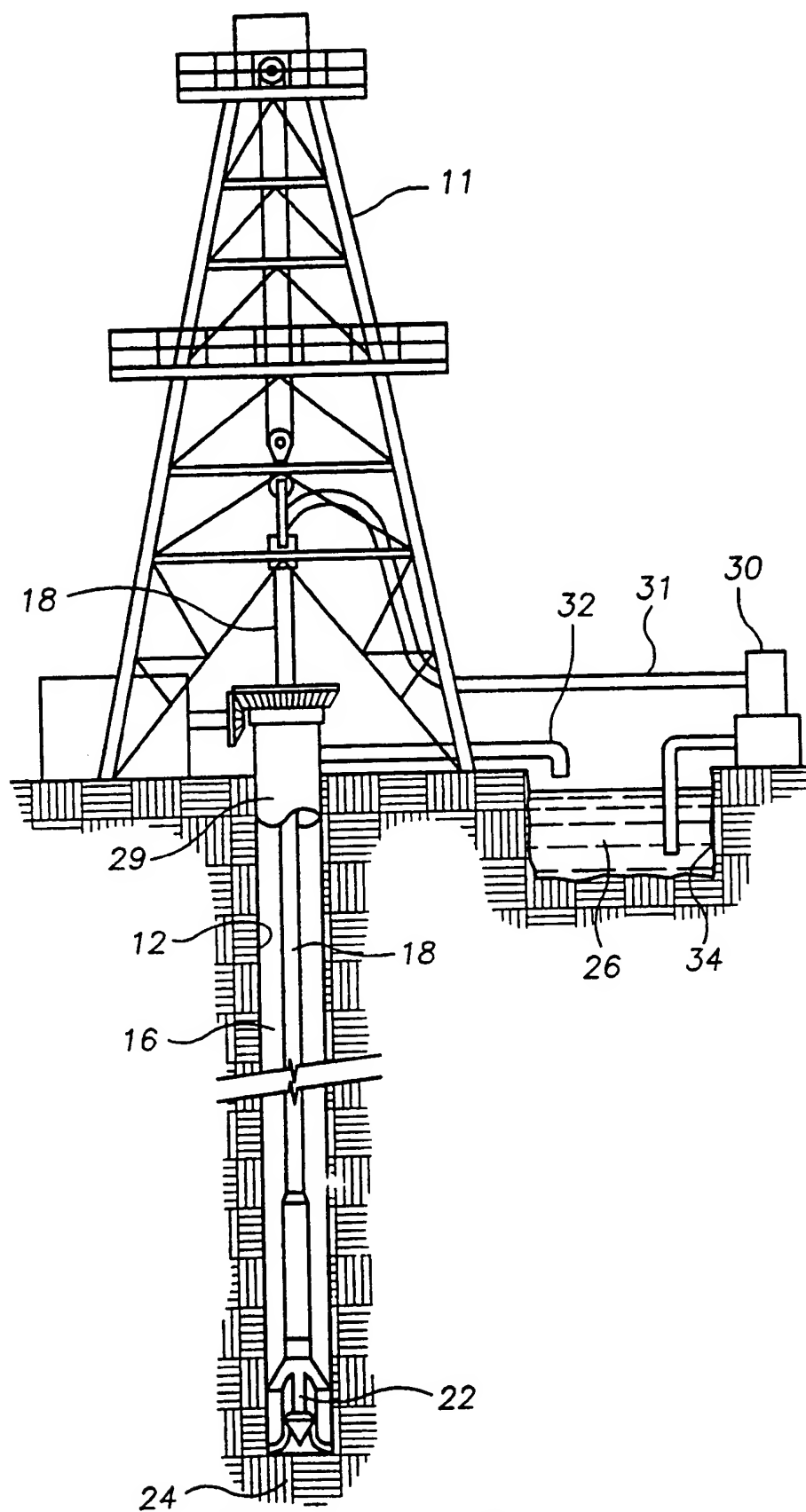


FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/11021

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K7/02 E21B33/138 C08F220/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- "&" document member of the same patent family

Date of the actual completion of the international search

17 September 1996

Date of mailing of the international search report

27.09.96

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INTERNATIONAL SEARCH REPORT

International Application No

US 96/11021

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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